

# Physicochemical Model and Kinetics of Pesticide Constituent Evaporation out of Multi-ingredient Polydisperse Aerosols<sup>‡</sup>

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**Abstract:** Contamination of the atmosphere by pesticides is an inevitable consequence of their application for plant protection, and a substantial part of pesticide pollutants exists as airborne particles. Evaporation of particulate matter is often the main pathway that provides the removal of intraparticle pesticide, and, thus, the detoxication of aerosol pollutants occurs. On the other hand, evaporation causes entry of pesticide vapour into the air, and may result in pesticide contamination of the atmosphere.

The known models of particle evaporation cannot be directly used for realistic multi-ingredient pesticide formulations because the data on the physicochemical properties of particle constituents are usually absent or unavailable. A simplified model is derived which describes the evaporation of the pesticide out of both an individual particle and a polydisperse aerosol mixture, taking into account the pesticide vapour pressure-temperature dependence, initial content of pesticide in particles, aerosol sizes, and degree of particle polydispersity, etc.. The temperature dependencies of evaporation rates for both the polydisperse aerosol mixtures, and the particles of diameter  $d_m \approx 2 \mu\text{m}$ , and, then, of an arbitrary diameter were determined for malathion, parathion-methyl, phosalone, propiconazole, and ethaphos formulations. The unknown vapour concentration or pressure-temperature dependencies were evaluated for some pesticides, and the evaporation life-times of particles were estimated under ambient conditions.

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## 1 INTRODUCTION

Contamination of the atmosphere by pesticides is an inevitable consequence of plant protection, and a substantial part of pesticide pollutants exists as airborne particles. Meteorological, chemical and environmental processes depend on whether a contaminant occurs as a liquid, a quasi-liquid (viscous), solid particles or vapour. Sunlight absorption and scattering, the rates of energy and charge transfers, as well as the diffusion rates of

reactive molecules, e.g. oxygen, within the particle bulk depend on both the particle size and the phase state, and, hence, the pathways and rates of chemical and photochemical decomposition are critically dependent on the substance state.<sup>1–3</sup> It is known also that the spatial and temporal distribution of atmospheric impurities, as well as the rates of dry and wet deposition of pollutants out of the atmosphere are influenced by their phase state and particle size.<sup>4</sup>

Evaporation of pesticides from particles is often the main pathway that provides the removal of intraparticle pesticide, resulting in the detoxication of aerosol pollutants. On the other hand, evaporation causes the entry of pesticide vapour into air, and may be one of the

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reasons for atmospheric pesticide contamination. Thus, the investigation of pesticide particle evaporation is important for environmental research, together with the atmospheric chemistry and the photochemistry of the pesticide. The study of aerosol evaporation is also necessary for the so-called Optimum Aerosol Technology of pesticide application<sup>3,5,6</sup> to estimate the potential evaporation losses inside a pesticide aerosol cloud moving by wind across a treated field.

Numerous publications deal with experimental measurements and theoretical calculations for droplet and aerosol evaporation. The evaporation and growth processes for particles containing a single substance have been analyzed by several investigators.<sup>7–10</sup> Although studies have been made of droplets containing multiple volatile and non-volatile substances, little consideration has been given to droplets with more than one volatile constituent.<sup>11–16</sup> Model calculations have mainly been carried out for particles of simple chemical composition (e.g. binary) with components of known physicochemical properties. However, commercial pesticides are mostly used in multi-ingredient formulations, and the composition, physicochemical and thermophysical properties of the ingredients are often unknown or unavailable. Thus, any reliable theoretical calculations are unsuitable for realistic pesticide formulations.

This paper describes a simplified physicochemical model based on the evaporation kinetics of the pesticide constituent. It also presents the experimental data on evaporation rates for a few pesticide formulations, for both polydisperse aerosol mixture and individual particles.

## 2 EXPERIMENTAL METHODS AND MATERIALS

### 2.1. Pesticides

The following pesticides were used in the experiments:

1. parathion-methyl as: (a) a commercial 400 g litre<sup>-1</sup> EC 'Metaphos' (Russia); (b) an experimental solution ( $\approx 280$  g litre<sup>-1</sup>) of pure parathion-methyl in *o*-xylene.
2. Malathion as an experimental formulation consisting of AI, 400 g litre<sup>-1</sup>, alkyl ether of polyethylene glycol (emulsifier) *c.* 100 g litre<sup>-1</sup> in Cellosolve as solvent.
3. Ethaphos [*O*-(2,4-dichlorophenyl) *O*-ethyl *S*-propyl thiophosphate] was provided by the Institute of Chemicals for Plant Protection, Moscow as: (a) an experimental formulation consisting of AI, 450 g litre<sup>-1</sup>, related impurities (e.g. *O*-(2,4-dichlorophenyl) *O*-ethyl *S*-ethyl thiophosphate), 20–30 g litre<sup>-1</sup>, the above-mentioned emulsifier, *c.* 100 g litre<sup>-1</sup> in isophorone as solvent; (b) a liquid technical product containing  $\approx 90\%$  AI,  $\approx 4$ –7% of

the above impurities, and  $\approx 3$ –6% of the emulsifier and solvent.

4. Phosalone as an experimental formulation consisting of AI, 350 g litre<sup>-1</sup>, the above emulsifier, *c.* 100 g litre<sup>-1</sup>, Cellosolve as solvent.
5. Propiconazole as a commercial 250 g litre<sup>-1</sup> EC 'Tilt' (Ciba-Geigy, Switzerland).

### 2.2 Pesticide analysis

For reasons of sensitivity and selectivity of pesticide analysis, gas-liquid chromatography was used to measure the above substances. A glass column of 3 mm ID, and of  $\approx 50$  cm length was packed with 5% SE-30 on Chromaton-N-AW-DMCS (0.16–0.2 mm). The argon carrier gas flow was set at 40 ml min<sup>-1</sup>, the column temperature was set within 200–240°C for different pesticides, and the temperature for an electron-capture detector (<sup>239</sup>Pu/<sup>3</sup>H type, Russia) was set at 230–250°C. The standard solutions of the above pure pesticides (parathion-methyl, malathion, phosalone), and of the commercial and technical products (propiconazole, ethaphos) were used to identify the chromatography peaks, and to measure pesticide amounts.

Capillary gas chromatography (a glass column 30 m  $\times$  0.2 mm ID, SE-30, a flame ionization detector, programmed temperature 70–280°C) was used to examine qualitatively the composition of pesticide formulations both before and after aerosol dispersion.

### 2.3 Experimental set-up and procedure

A schematic view of the experimental set-up is shown in Fig. 1. It consists of an aerosol chamber 30  $\times$  30  $\times$  40 cm (1), aerosol pneumatic nozzle sprayer (2) with a compressed air supply, vertical stainless steel tube-vaporizer (3) of 4 cm ID, and of  $\approx 170$  cm length, with a few separate electric spiral heaters (4) around the tube, and overall oven (5) with electric heater (6) and air fan (7). Filter holder (8) with polymeric thin-fibrous filters (AFACHA-20, Russia), and air pump (9) are fixed on the bottom of the tube. A flow of either pure air (from the room), or air containing pesticide aerosols (from the aerosol chamber) can enter the tube by a bypass-valve (10). The volume flow rate (6–14 litre min<sup>-1</sup>) is measured by a gas rotameter (11), and is controlled by pump and flow regulator (12). Seven thermocouples (13) are used to measure bulk temperatures in various sections of the tube. The use of separate tube heaters together with the oven allows the temperature to be varied (within 50–150°C), whilst maintaining even temperatures along the tube ( $\delta T \approx 0.5$ –3°C). The temperature at the entrance and exit must be lower to prevent uncontrolled aerosol evaporation under the valve-induced flow turbulence conditions, and on the filters. Average value of tem-

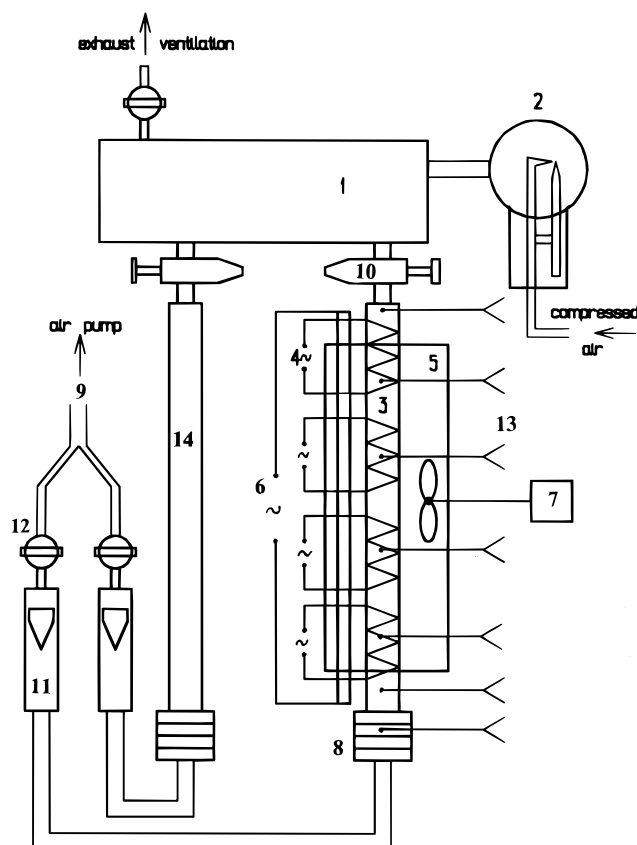


Fig. 1. Schematic view of the experimental set-up.

perature  $T$  for the hot parts of the vaporizer is calculated as

$$1/T = (\sum (1/T_k))/K$$

where  $T_k$  are the temperatures measured by the thermocouples at four sites in the hot tube ( $k = 4$ ). Parallel bypass-valve, filter holder, rotameter, flow regulator, and the tube (but without any heaters) are used to carry out comparative measurements, and are marked jointly as (14) in Fig. 1.

The experimental procedure was as follows: Even flows of pure air were established through the vaporizer and parallel tube, and a given temperature  $T$  established in the vaporizer (room temperature in the comparative tube). A pesticide formulation was dispersed by a pneumatic (Collison's) nozzle sprayer,<sup>17</sup> and aerosols introduced into the chamber by a rubber tube. A suitable aerosol pesticide concentration in the chamber ( $0.2\text{--}3 \mu\text{g litre}^{-1}$ ) was established, using a few preliminary samplings of aerosols followed by the pumping of surplus of aerosols out of the chamber. The even flows of 'air + aerosols' out of the chamber were simultaneously connected to both the vaporizer and comparative tube for a few seconds (5–20 s) using the above bypass-valves. Then the reverse connections to the above pure air flows were performed. Thus, one aerosol sample (0.5–2 litres) moved through the hot vaporizer, and a pesticide constituent partly evaporated out of

particles; the remaining aerosols were then collected on the filter. The identical aerosol sample moved in the comparative tube at room temperature without a marked loss through evaporation, and was collected on the comparative filter. The filters were placed into glass test-tubes with 1–5 ml of hexane + ether (1 + 1 by volume), and the extracts analyzed by gas chromatography. The amount of pesticide present on the comparative filter may be considered as the initial amount of aerosol pesticide at the tube-vaporizer entrance,  $\Omega_{a0}$ , and pesticide remaining on the vaporizer filter may be adopted as the final amount,  $\Omega_a(T, t)$ . One may determine the time/temperature dependence for the evaporation depth

$$\Phi(T, t) = \Omega_a(T, t)/\Omega_{a0}$$

by varying the vaporizer temperature  $T$  (50–120°C), linear flow speed ( $8\text{--}24 \text{ cm s}^{-1}$ ), and, hence, time  $t$  (5–20 s).

### 3 PHYSICOCHEMICAL EVAPORATION MODEL

#### 3.1 Model assumptions, derivation of model equations and relationships

The heat and mass transfer equations for the evaporation of multi-ingredient particles cannot be solved mathematically for arbitrary particles, and for realistic intraparticle compositions. Numerical computations would also require information about internal diffusion as well as external diffusion rates of any particle constituent, rates of internal and external heat transfers, and data on the physicochemical properties of mixture species. As was mentioned above, such data are unavailable for pesticide formulations. Nevertheless, it is possible to derive a simplified model which describes only the evaporation rate of a pesticide constituent out of a particle.<sup>18,19</sup>

Numerous theoretical and experimental studies<sup>7,11–14</sup> show that it is possible to use the quasi-steady-state approximation for evaporation, together with the following assumptions:

- temperature difference between evaporating particles and ambient air is negligible;
- Stefan's flow is negligible;
- the effect of relative movement of particle and air on evaporation rate is negligible;
- the effect of surface curvature on vapour pressure (Kelvin's effect) can be ignored;
- the rates of intraparticle heat transfer are large in relation to the evaporation rate;
- intraparticle mass transport processes are fast in relation to the evaporation process;
- species vapour pressures are modelled according to Raoult–Henry's law.

Any commercial pesticide formulation, besides a defined pesticide constituent contains many other ingredients, e.g. solvents, emulsifiers, emulsion stabilizers, and various minor impurities (more than 20 recognized and unrecognized substances were found in the above formulations by capillary gas-liquid chromatography). The relatively volatile solvents must evaporate shortly after spraying, and, thus, the particles must consist under laboratory or field conditions only of relatively non-volatile substances. Taking into account the above assumptions, for such a multi-ingredient spherical particle it can be reasonably assumed that Fick's diffusion (evaporation) equation<sup>7,11</sup> has a modified quasi-stationary steady-state solution for a pesticide mass flux  $J(t)$ :

$$J(t) = -\frac{\delta m}{\delta t} = 2\pi d(t)DC_s(T)x(t) \quad (1)$$

Here  $t$  (s) is the time;  $J(t)$  ( $\text{g s}^{-1}$ ) is the pesticide mass flux moving away from the evaporating particle;  $d(t)$  (cm) is the particle diameter at time  $t$ ;  $D$  ( $\text{cm}^2 \text{s}^{-1}$ ) is the diffusivity of pesticide vapour in ambient air;  $C_s(T)$  ( $\text{g cm}^{-3}$ ) is the saturated vapour concentration of pure pesticide substance at temperature  $T$  ( $^{\circ}\text{K}$ ); and  $x(t)$  is the mole fraction of pesticide species in the evaporating particles at time  $t$ , given by

$$x(t) = (m_p(t)/M_p) / \{m_p(t)/M_p + \sum (m_n(t)/M_n)\} \quad (2)$$

where  $m_p$ ,  $M_p$ ,  $m_n$ ,  $M_n$  are the masses (g), and molecular weights ( $\text{g mole}^{-1}$ ) of pesticide and non-pesticide ingredients, respectively.

Two extreme cases for particle composition can be assumed. In the first, after fast evaporation of volatile solvents, the remaining particle consists of almost pure pesticide. Hence,  $x \approx 1$ , and Maxwell–Langmuir's solution<sup>7,11,14</sup> (the so-called  $d$ -squared law;<sup>7,14</sup> the subscript (d) will indicate the  $d$ -squared evaporation law) may be used for eqn (1):

$$m_p(t) \approx m_{p0} \{1 - (8DC_s(T)/\rho d_0^2)t\}^{3/2} = m_{p0} \{1 - t/\tau_d\}^{3/2} \quad (3)$$

where  $m_{p0}$  is the initial ( $t = 0$ ) mass of pesticide constituent in the particle,  $\rho$  ( $\text{g cm}^{-3}$ ) is the density of particle material. As follows from expression (3), the characteristic time for full evaporation of a particle with an initial diameter  $d_0$  is:

$$\tau_d = \rho d_0^2 / 8DC_s(T) \quad (3a)$$

In the second case the non-pesticide ingredients are assumed to be non-volatile (i.e.  $m_n(t) \approx \text{const} \approx m_{n0}$ , where  $m_{n0}$  is the initial mass of any non-pesticide ingredient), but a relatively volatile pesticide is assumed

to be minor in the particle bulk. Obviously, even after full evaporation of the pesticide constituent the overall particle mass and diameter might change negligibly. Hence, the denominator in eqn (2) may be rewritten as:

$$\begin{aligned} m_p(t)/M_p + \sum (m_n(t)/M_n) \\ \approx \sum (m_n(t)/M_n) \approx \sum (m_{n0}/M_n) \approx \text{const} \end{aligned} \quad (4)$$

and

$$d(t) \approx \text{const} \approx d_0 \quad (4a)$$

From expressions (1, 2, 4, and 4a) the following equation can be obtained:

$$\begin{aligned} (m_p(t) - m_{p0})/M_p + \sum (m_{n0}/M_n) \ln(m_p(t)/m_{p0}) \\ = -(2\pi d_0 DC_s(T)/M_p)t \end{aligned} \quad (5)$$

It can be estimated that for a minor initial pesticide content ( $\leq 30\%$ ) the first term in eqn (5) may be ignored. Let us also assume that the molecular weights of non-pesticide ingredients are very similar, and their average value is  $M$ , so that the total particle mass will be approximately the sum of the masses of non-pesticide ingredients, and, hence:

$$\sum (m_{n0}/M_n) \approx (\sum m_{n0})/M \approx \rho \pi d_0^3 / 6M \quad (6)$$

Thus, expression (5) can be written as:

$$\begin{aligned} m_p(t) \approx m_{p0} \exp(-12DC_s(T)Mt/\rho d_0^2 M_p) \\ = m_{p0} \exp(-t/\tau_e) \end{aligned} \quad (7)$$

The characteristic time  $\tau_e$  for such exponential evaporation law (the subscript (e) indicates here the exponential evaporation law):

$$\tau_e = \rho d_0^2 M_p / (12DC_s(T)M) \quad (7a)$$

is close to the similar one  $\tau_d$  for the  $d$ -squared law ( $M/M_p$  ratio in eqn (7a) can be assumed as 1–1.5). Note also that for deep exponential evaporation it is necessary to take a time interval  $t \approx (2 \div 3)\tau_e$ . Thus, we obtain almost coincident times for full evaporation of particles that consists of an almost pure pesticide (the  $d$ -squared law), and for practically full exponential evaporation of a minor pesticide constituent out of the above multiingredient particle.

### 3.2 Evaporation laws for arbitrary particle composition

The results obtained for both extreme cases, i.e. for high and low intraparticle pesticide contents, show that the characteristic evaporation times,  $\tau_d$  and  $\tau_e$ , almost coincide with each other, and are equally dependent on both the particle size,  $d$ , and the physicochemical properties

of substances,  $\rho$ ,  $D$ ,  $C_s(T)$ . Moreover, despite different mathematical forms of eqns (3) and (7), their plots seem very close to each other up to an evaporation depth of 70–85%. This conclusion permits us to postulate that eqns (3) or (7) may formally describe an evaporation process for any particle composition. Thus, eqns (3), (3a), and (7), (7a) are used in the present study to interpret the experimental evaporation data for the investigated pesticide formulations, to predict the fates of pesticide particles in the atmosphere, and to evaluate unknown vapour-temperature dependencies for some pesticides.

### 3.3 Time-temperature dependence of evaporation kinetics

As described in Section 2.3, the experimental procedure permits measurement of the initial,  $\Omega_{a0}$ , and final,  $\Omega_a(T, t)$ , pesticide amounts for various temperatures  $T$ , and times  $t$ . Taking into account the above postulated overall evaporation laws as eqns (3) or (7), one may write the expressions for the evaporation depth  $\Phi(T, t) = \Omega_a(T, t)/\Omega_{a0}$  as:

$$\Phi_d(T, t) = \{1 - 8DC_s(T)t/\rho d_0^2\}^{3/2} = \{1 - t/\tau_d\}^{3/2} \quad (8)$$

$$\Phi_e(T, t) = \exp(-12DC_s(T)Mt/\rho d_0^2 M_p) = \exp(-t/\tau_e) \quad (9)$$

The value  $t$  might be determined as a ratio of the hot tube length,  $L$ , to 'air + aerosols' flow speed,  $V$ , which might be calculated as a ratio of volume flow rate,  $Q$ , to tube cross-section,  $S$ . However, a laminar (Poiseuille's) 'air + aerosols' flow exists in the tube<sup>20</sup> with a parabolic radial dependence of speed,  $V(r) = V_{\max}[1 - r/r_0]^2$ , where  $r$  is the current tube radial coordinate;  $r_0 = 2$  cm is the inner tube radius;  $V_{\max} = 2Q/S$  is the 'air + aerosol' speed near tube axis. It results in different times of aerosol passage, and, hence, different evaporation depths in various cross-section parts. Thus, it is necessary to modify expressions (8) and (9) by their cross-section integration, and the following relationships may be obtained:

$$\begin{aligned} \Phi_d &= \int_0^{r_0} (2\pi r \delta r V(r)) \left[ 1 - \frac{(L/V(r))}{\tau_d} \right]^{3/2} \\ &= (1 - \tau/\tau_d)^{3/2} - \frac{3}{2}(\tau/\tau_d)\sqrt{1 - \tau/\tau_d} \\ &\quad + \frac{3}{4}(\tau/\tau_d)^2 \ln \frac{1 + \sqrt{1 - \tau/\tau_d}}{1 - \sqrt{1 - \tau/\tau_d}} \end{aligned} \quad (10)$$

$$\begin{aligned} \Phi_e &= \int_0^{r_0} (2\pi r \delta r V(r)) \exp\left(-\frac{(L/V(r))}{\tau_e}\right) \\ &= \exp(-\tau/\tau_e) - (\tau/\tau_e)\exp(-\tau/\tau_e) - (\tau/\tau_e)^2 \text{Ei}(-\tau/\tau_e) \end{aligned} \quad (11)$$

Here  $\text{Ei}(-\tau/\tau_e)$  is the so-called exponential integral;<sup>21</sup> notation  $\tau = L/V_{\max}$  is a time parameter, which will be used below instead of at a concrete time interval  $t$ , which becomes useless due to the different times of aerosol passage through various cross-section parts.

The temperature expansion for the air which passes from the relatively cold aerosol chamber into the hot tube must also be taken into account. It results in an increase in the speed of 'air + aerosol' flow in the hot tube, and the above time  $\tau = L/V_{\max}$  must be rewritten as

$$\tau = (T_0/T)(L/V_{\max}) = T_0 LS/2TQ$$

where  $T_0$  is room temperature.

Thus, the next algorithm must be used to interpret the tube evaporation data for the above samples of pesticide aerosols in the tube-vaporizer. For any experiment, the values of  $T$ ,  $T_0$ ,  $Q$ ,  $\Omega_{a0}$ ,  $\Omega_a(T, \tau)$ ,  $L$ ,  $\tau$ , and  $\Phi = \Omega_a(T, \tau)/\Omega_{a0}$  are experimentally determined. Preliminary calculations have been made of expressions (10), and (11) for various ratios of  $\tau/\tau_d$  and  $\tau/\tau_e$  ( $0 \leq \tau/\tau_d \leq 1$ ,  $0 \leq \tau/\tau_e \leq 4$ ), and are used as the calibration graphs. By comparing with the above calibration graphs, one may determine from the experimental data of  $\Phi$  and  $\tau$  the characteristic evaporation times of interest,  $\tau_d$  and  $\tau_e$ , at temperature  $T$ . From relationships (3a) and (7a), the temperature dependence of  $\tau_d$  or  $\tau_e$  is related to a pesticide vapour concentration-temperature dependence,  $C_s(T)$ . It is known that a vapour concentration-temperature relationship may be written as:<sup>22</sup>

$$C_s(T) = C_0 \exp(-H_{\text{eff}}/T) \quad (12)$$

where  $C_0$  is a formal pre-exponential factor.  $H_{\text{eff}}$  is the effective latent heat of vaporization (in temperature units, K) for a given pesticide, and is lower by approximately the value of  $T$  than the true heat  $H_{\text{tr}}$  in a similar relationship for vapour pressure dependence  $P_s(T) = P_0 \exp(-H_{\text{tr}}/T)$ .<sup>22</sup> Hence, relationships (3a) and (7a) can be written as:

$$\tau_d = (\rho d_0^2/8DC_0)\exp(H_{\text{eff}}/T) \quad (13)$$

$$\tau_e = (\rho d_0^2 M_p/12DC_0 M)\exp(H_{\text{eff}}/T) \quad (14)$$

The last relationships are nominally similar to the equations for the characteristic times (rates) of chemical reactions (the Arrhenius equations),<sup>2</sup> and the semi-logarithmic plots (the Arrhenius plots)<sup>2</sup>  $\ln \tau_d$  or  $\ln \tau_e$  vs  $1/T$ , may be used to determine experimentally the latent heats  $H_{\text{eff}}$  (as a slope of straight line), and the pre-exponential factors (as an intercept on the  $\ln \tau_d$ , or  $\ln \tau_e$  axes). Thus, the temperature dependencies of characteristic evaporation times,  $\tau_d$ , and  $\tau_e$ , for the above samples of pesticide aerosols can be found.

### 3.4 Aerosol polydispersity, evaporation kinetics for mixture of polydisperse aerosols, and for individual particles

It would be desirable to measure separately the evaporation rates of monodisperse aerosols with diameters of interest within 1–50  $\mu\text{m}$ . However, it is difficult or even impossible in practice to produce such monodisperse particles from toxic pesticide formulations using the aerosol devices which are usually suitable for simple liquids, mainly water, water + glycerine, dibutyl phthalate, and similar compounds. On the other hand, polydisperse pesticide aerosols and droplets are used in the field treatments of crops, and polydisperse particulate matter exists permanently in the atmosphere. Thus, the study of evaporation kinetics of various polydisperse aerosol systems is important if we are to understand how pesticides contaminate the atmosphere.

Simultaneous evaporation of small and large particles must artificially disturb the temperature dependence of evaporation kinetics for such polydisperse mixtures compared to the true one for a group of monodisperse particles. The reason for such disturbance is that the characteristic evaporation time  $\tau_d$  or  $\tau_e$  is proportional to  $d^2$ , i.e. the time is much longer for large particles than for small ones. Small particles could evaporate almost completely at a certain temperature, whilst large particles would remain largely unaltered. Hence, an increase in mixture temperature could cause only a little additional overall evaporation depth for such a system, and the slope of the straight line Arrhenius plot must be artificially lower for the aerosol mixture than the expected  $H_{\text{eff}}$  value for a given pesticide, although each kind of aerosol evaporates according to the true expressions (3a) or (7a) with the above  $H_{\text{eff}}$  value. It is the essential conclusion that the evaporation temperature kinetics for a mixture of polydisperse aerosols characterizes evaporation of the mixture taken as a whole, but not of any individual particle from the mixture.

As was pointed out in Section 2.3 a pneumatic sprayer was used to produce pesticide aerosols. Using the particle analyzer (APPA type, Russia) it has been found that the size distribution was the standard 'log-normal' one:<sup>17</sup>

$$F(d) \delta d = \frac{1}{\sqrt{2\pi}} \exp(-u^2/2) \delta u \quad (15)$$

$$u = \ln(d/d_m)/\ln \sigma_g \quad (16)$$

Here  $F(d) \delta d$  is the fraction of substance mass which is contained in particles with diameters from  $d$  to  $d + \delta d$ ;  $d_m$  is the mass-median diameter,<sup>17</sup> i.e. half of the substance is contained in particles with  $d < d_m$ , and the other half in particles with  $d > d_m$ . Parameter  $\sigma_g$  is the geometric standard deviation of particle sizes for a poly-

disperse system ( $\sigma_g = 1$  for a monodisperse system). In the experiments  $d_m \approx 2.03 (\pm 0.14) \mu\text{m}$ ,  $\sigma_g \approx 1.8 (\pm 0.1)$ , and, hence,  $\approx 68\%$  of substance was contained in particles with diameters from  $1.1 \mu\text{m}$  ( $d_m/\sigma_g$ ) to  $3.6 \mu\text{m}$  ( $d_m \sigma_g$ ), and  $\approx 95\%$  from  $0.6 \mu\text{m}$  ( $d_m/\sigma_g^2$ ) to  $6.5 \mu\text{m}$  ( $d_m \sigma_g^2$ ).

The experimental algorithm described in Section 3.3 is undoubtedly valid for the evaporation kinetics of a polydisperse aerosol mixture, and, hence, the obtained results must characterize its overall evaporation. Nevertheless, it is also possible from the same experimental data to calculate the evaporation rates for a hypothetical individual particle of diameter  $d_m$  ( $\approx 2.03 \mu\text{m}$  in this study), and, then, of any particle diameter. For this purpose the polydispersity expression (15) for an aerosol mixture must be doubly integrated with the evaporation expression ((3) or (7)) for an individual particle of current diameter  $d$ , and with the above parabolic radial profile of 'air + aerosols' speed. Using expression (16), written as  $d = d_m \exp(u \ln \sigma_g)$ , the following expressions are obtained:

$$\begin{aligned} \phi_d &= \int_0^{r_0} \left\{ \int_{d_{\min}}^{\infty} \left[ 1 - \frac{L}{V(r)\tau_d(d)} \right]^{3/2} F(d) \delta d \right\} 2\pi r V(r) \delta r \\ &= \int_0^{r_0} \left\{ \frac{1}{\sqrt{2\pi}} \int_{u_{\min}}^{\infty} \exp(-u(r)^2/2) \right. \\ &\quad \times \left. \left[ 1 - \frac{L}{V(r)\tau_d(d_m)} \exp(-2u(r) \ln \sigma_g) \right]^{3/2} \delta u \right\} \\ &\quad \times 2\pi r V(r) \delta r \end{aligned} \quad (17)$$

$$\begin{aligned} \phi_e &= \int_0^{r_0} \left\{ \int_0^{\infty} \exp\left(-\frac{L}{V(r)\tau_e(d)}\right) F(d) \delta d \right\} 2\pi r \delta r V(r) \\ &= \int_0^{r_0} \left\{ \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \exp(-u(r)^2/2) \right. \\ &\quad \times \exp\left(-\frac{L}{V(r)\tau_e(d_m)} \exp(-2u(r) \ln \sigma_g)\right) \delta u \left. \right\} \\ &\quad \times 2\pi r V(r) \delta r \end{aligned} \quad (18)$$

Here  $\phi_d$  and  $\phi_e$  are the notations for the calculated depths for the polydisperse system evaporating into the hot tube-vaporizer according to expressions (3) and (7), respectively. Notations  $\tau_d(d_m)$ ,  $\tau_d(d)$ ,  $\tau_e(d_m)$ , and  $\tau_e(d)$  are the characteristic evaporation times for the individual particles of diameter  $d_m$  or of current diameter  $d$ , respectively. The lower limit of integration

$$u_{\min} = \ln\left(\frac{L}{V(r)\tau_d(d_m)}\right) / 2 \ln \sigma_g$$

in (17) means that all particles with diameters less than  $d_m \exp(u_{\min} \ln \sigma_g)$  evaporate completely in the vaporizer.

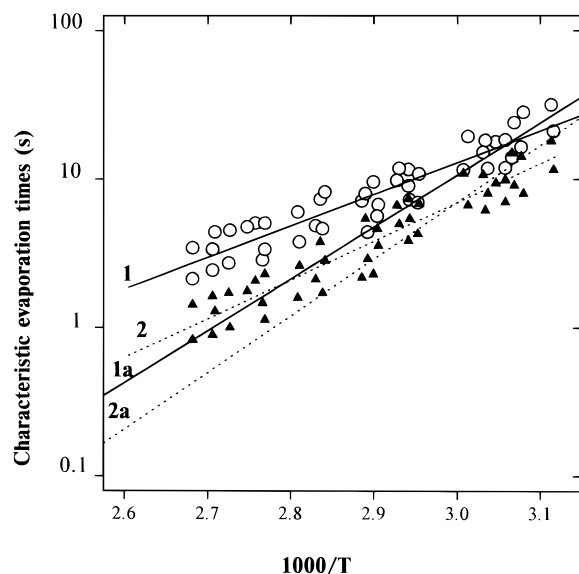
The relationships (omitted here) which are close to expressions (10) or (11) were obtained for integrals (17)

or (18), and used as the calibration graphs. Thus, apart from the algorithm described earlier for the overall evaporation kinetics of polydisperse mixture, the same experimental data,  $\Phi = \Omega_a(T, \tau)/\Omega_{a0}$ , must be compared with the above calibration graphs,  $\phi_d$  and  $\phi_e$ . In this way the needed temperature dependencies of characteristic times,  $\tau_d(d_m)$  and  $\tau_e(d_m)$ , for a particle of diameter  $d_m$  can be found. As follows from expressions (13, 14), the factor  $d^2/d_m^2$  must be used for an arbitrary diameter  $d$ .

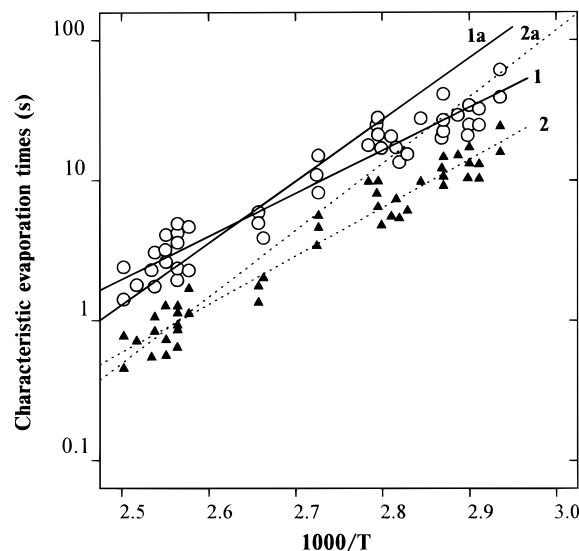
## 4 EXPERIMENTAL RESULTS AND DISCUSSION

### 4.1 Experimental evaporation plots and dependencies

The experimental temperature dependencies of evaporation times,  $\tau_d$  and  $\tau_e$ , for two pesticides (malathion and propiconazole) as the mixtures of polydisperse aerosols are shown in Figs 2 and 3. The calculated ones,  $\tau_d(d_m)$  and  $\tau_e(d_m)$ , for individual particles of  $d_m = 2.03 \mu\text{m}$  are also shown here. The principal conclusion (Section 3.4) is confirmed, that a time-temperature dependence for a mixture of polydisperse aerosols characterizes the evaporation kinetics of the mixture itself, but not of any individual particle from the mixture (as the slopes of straight lines are essentially different, compare lines 1 and 1a, or 2 and 2a in the figures). The plots for both parathion-methyl formulations are presented in Fig. 4. As is seen from Fig. 4, there is a small influence of pesticide formulation on the evaporation rates, and, hence, the postulated evaporation expres-



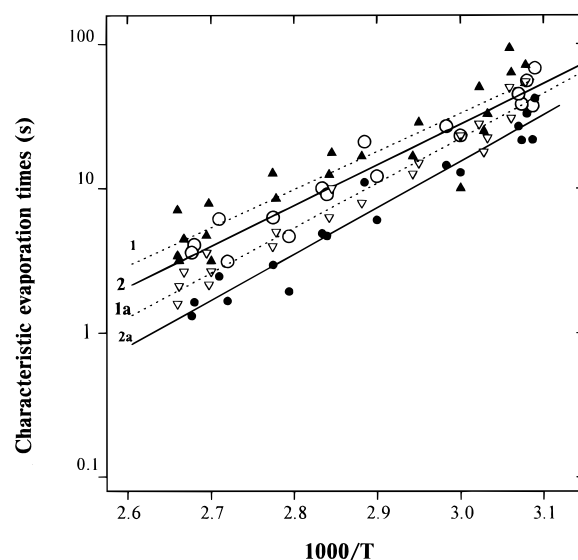
**Fig. 2.** Experimental data and fitted temperature dependencies of characteristic evaporation times  $\tau_d$  (solid line 1, symbol  $\circ$ ) and  $\tau_e$  (dotted line 2,  $\blacktriangle$ ) for the polydisperse system of malathion aerosols, and the calculated ones for the individual malathion particle of diameter  $d_m = 2.03 \mu\text{m}$  (solid line 1a—for  $\tau_d$ , dotted 2a—for  $\tau_e$ ).



**Fig. 3.** Experimental data and fitted temperature dependencies of characteristic evaporation times  $\tau_d$  (solid line 1, symbol  $\circ$ ) and  $\tau_e$  (dotted line 2,  $\blacktriangle$ ) for the polydisperse system of propiconazole aerosols, and the calculated ones for the individual propiconazole particle of diameter  $d_m = 2.03 \mu\text{m}$  (solid line 1a—for  $\tau_d$ , dotted line 2a—for  $\tau_e$ ).

sions (Section 3.2) for an arbitrary particle composition might be adopted.

Similar plots were obtained for other substances, and the summary information on the evaporation times is listed in Table 1. The results for the polydisperse mixtures are presented in the form  $10^A \exp(G/T)$ , where  $A$  and  $G$  are the formal parameters, fitted by the Least Squares Fitting to the experimental kinetics. The data on the individual particles of  $d_m = 2.03 \mu\text{m}$  are presented in a similar form,  $10^B \exp(H/T)$ . Here parameter  $H$  is



**Fig. 4.** Experimental data and fitted temperature dependencies of characteristic evaporation times for the polydisperse aerosols produced from two parathion-methyl formulations: dotted line 1, symbol  $\blacktriangle$ — $\tau_d$ , formulation (b); solid line 2,  $\circ$ — $\tau_d$ , formulation (a); dotted line 1a,  $\nabla$ — $\tau_e$ , formulation (b); solid line 2a,  $\bullet$ — $\tau_e$ , formulation (a).

**TABLE 1**  
Temperature Dependencies of Characteristic Evaporation Times

Pesticide	Temperature range (K)	Characteristic evaporation times $\tau_d$ and $\tau_e$ (s) <sup>a</sup>			
		Polydisperse system		Individual particle of diameter $d_m = 2.03 \mu\text{m}$	
		A ( $\pm$ SD)	G ( $\pm$ SD)	B ( $\pm$ SD)	H ( $\pm$ SD)
Malathion	320–370	$\tau_d$ : $-5.3 (\pm 0.4)$ $\tau_e$ : $-7.1 (\pm 0.4)$	4880 ( $\pm 300$ ) 6020 ( $\pm 340$ )	$-9.6 (\pm 0.6)$ $-10.7 (\pm 0.6)$	8050 ( $\pm 460$ ) 8800 ( $\pm 490$ )
Parathion-methyl	320–380	$\tau_d$ : $-7.0 (\pm 0.5)$ $\tau_e$ : $-8.4 (\pm 0.5)$	6460 ( $\pm 400$ ) 7380 ( $\pm 440$ )	$-10.1 (\pm 0.7)$ $-11.2 (\pm 0.7)$	9000 ( $\pm 550$ ) 9585 ( $\pm 490$ )
Formulation (a)		$\tau_d$ : $-6.5 (\pm 0.8)$ $\tau_e$ : $-8.0 (\pm 0.4)$	6130 ( $\pm 640$ ) 7130 ( $\pm 320$ )	$-9.9 (\pm 0.8)$ $-11.0 (\pm 0.8)$	8870 ( $\pm 660$ ) 9525 ( $\pm 670$ )
Formulation (b)		$\tau_d$ : $-10.4 (\pm 0.8)$ $\tau_e$ : $-12.4 (\pm 0.8)$	9600 ( $\pm 570$ ) 11000 ( $\pm 600$ )	$-13.7 (\pm 0.8)$ $-14.6 (\pm 0.8)$	12440 ( $\pm 680$ ) 12940 ( $\pm 650$ )
Phosalone	345–390	$\tau_d$ : $-6.4 (\pm 0.4)$ $\tau_e$ : $-8.0 (\pm 0.4)$	5920 ( $\pm 300$ ) 6960 ( $\pm 300$ )	$-9.8 (\pm 0.4)$ $-11.0 (\pm 0.8)$	8690 ( $\pm 360$ ) 9380 ( $\pm 300$ )
Ethaphos	330–380	$\tau_d$ : $-6.2 (\pm 0.5)$ $\tau_e$ : $-8.0 (\pm 0.6)$	5840 ( $\pm 440$ ) 7000 ( $\pm 550$ )	$-10.1 (\pm 0.9)$ $-11.2 (\pm 1.0)$	8980 ( $\pm 770$ ) 9590 ( $\pm 810$ )
Formulation (a)		$\tau_d$ : $-7.4 (\pm 0.4)$ $\tau_e$ : $-8.8 (\pm 0.4)$	7080 ( $\pm 300$ ) 7930 ( $\pm 280$ )	$-10.9 (\pm 0.6)$ $-12.2 (\pm 0.7)$	10130 ( $\pm 520$ ) 10940 ( $\pm 490$ )
Formulation (b)					
Propiconazole	340–385				

<sup>a</sup> Presented as  $10^A \exp(G/T)$  or  $10^B \exp(H/T)$ .

expected to be close to the effective latent heat of vaporization for the given pesticide. Notation  $10^B$  means here a formal pre-exponential factor, but it may be connected with the evaporation parameters established from the following equations:

$$10^B \approx \rho d_m^2 / 8DC_0, \quad \text{or} \quad 10^B \approx \rho d_m^2 M_p / 12DC_0 M \quad (19)$$

where  $d_m \approx 2.03 \times 10^{-4} \text{ cm}$  ( $2.03 \mu\text{m}$ ). As follows from expression (19), the factor  $d^2/(2.03)^2$  must additionally be introduced into the pre-exponential factors  $10^B$  (Table 1) for an arbitrary particle diameter  $d$  (in  $\mu\text{m}$ ).

#### 4.2 Comparison of measured and calculated characteristic evaporation times, and examination of evaporation model validity

It seems possible from expressions (13) or (14) to calculate theoretically the evaporation times for the particles produced from pesticides whose  $C_s(T)$ , or  $P_s(T)$  dependencies are known. For instance, the following expressions can be obtained for  $C_s(T)$  from the reference data on vapour pressure for parathion-methyl and malathion:

$$C_s(T) = C_0 \exp(-H_{\text{eff}}/T) \approx 10^{3.6} \exp(-8290/T) \text{—malathion}^{23} \quad (20)$$

$$\approx 10^{5.5} \exp(-10360/T) \text{—parathion-methyl}^{23} \quad (21)$$

$$\approx 10^{3.4} \exp(-8800/T) \text{—parathion-methyl}^{24} \quad (22)$$

Apart from the measured or estimated values of  $\rho$  ( $\approx 1.3 \text{ g cm}^{-3}$ ),  $d_m$  ( $\approx 2.03 \times 10^{-4} \text{ cm}$ ),  $M/M_p$  ( $\approx 1.1$ ), and  $C_s(T)$  (expressions 20, 21 or 22), the diffusivity of pesticide vapour in air,  $D$ , must be used. It can be calculated using the method described in Reference 22. For malathion it may be presented as:

$$D \approx D_m(T/T_m)^{3/2}$$

where  $D_m = 0.053 \text{ cm}^2 \text{ s}^{-1}$  and  $T_m = 345^\circ \text{K}$  is the mid-point of the temperature range for malathion experiments; similar data for parathion-methyl are  $0.067 \text{ cm}^2 \text{ s}^{-1}$ , and  $350^\circ \text{K}$ . It is seen that the diffusivity itself has the temperature factor  $T^{3/2}$ , and, hence,  $\tau_d$  and  $\tau_e$  are proportional to  $T^{-3/2} \exp(H_{\text{eff}}/T)$ . It can be shown that expressions (13), and (14) with such a complex temperature dependence may be transformed into the following forms:

$$\tau_d = \left( \frac{\rho d_m^2}{8D_m C_0} \right) \left( \frac{T_m}{T} \right)^{3/2} \exp\left( \frac{H_{\text{eff}}}{T} \right) \approx \left( \frac{\rho d_m^2}{8D_m C_0} \right) \exp\left( -\frac{3}{2} \right) \exp\left[ \frac{H_{\text{eff}} + (3/2)T}{T} \right] \quad (24)$$

$$\tau_e = \left( \frac{\rho d_m^2 M_p}{12D_m C_0 M} \right) \left( \frac{T_m}{T} \right)^{3/2} \exp\left( \frac{H_{\text{eff}}}{T} \right) \approx \left( \frac{\rho d_m^2 M_p}{12D_m C_0 M} \right) \exp\left( -\frac{3}{2} \right) \exp\left[ \frac{H_{\text{eff}} + (3/2)T}{T} \right] \quad (24a)$$



Hence, the theoretical dependencies  $\tau_d$  and  $\tau_e$  for malathion may be calculated as:

$$\tau_d(d_m = 2.03 \mu\text{m}) \approx 10^{-11.2} \exp(8815/T) \text{ (s)}$$

and

$$\tau_e \approx 10^{-11.4} \exp(8810/T) \text{ (s)}$$

whereas the experimental values are

$$\tau_d = 10^{-9.6} \exp(8050/T) \quad \text{and}$$

$$\tau_e = 10^{-10.7} \exp(8800/T)$$

respectively (Table 1; the standard errors of reference and experimental data are omitted). Similar results are obtained for parathion-methyl, using the average experimental values for both parathion-methyl formulations (Table 1), and  $C_s(T)$  as relation (22):

$$\tau_d = 10^{-11.1} \exp(9325/T)$$

$$\text{and } \tau_e = 10^{-11.3} \exp(9325/T) \text{—calculated values;}$$

$$\tau_d = 10^{-10.0} \exp(8935/T)$$

$$\text{and } \tau_e = 10^{-11.1} \exp(9555/T) \text{—experimental values}$$

One should note that the calculated and experimental dependencies have close latent heats for malathion and parathion-methyl, especially for the exponential evaporation law (8810 K and 9325 K against 8800 K and 9555 K, respectively). However, the calculated values of  $\tau_d$ , and  $\tau_e$  are usually 2–4 times lower than the experimental ones, and an additional dimensionless factor must be included in expressions (3), (7), (24), and (24a) to establish agreement between experimental and theoretical rates. On the other hand, the reference data on  $P_s(T)$  or  $C_s(T)$  may be not sufficiently reliable for the theoretical calculations (compare expressions (21) and (22) for parathion-methyl). Nevertheless, one may observe an underlying agreement (see also Section 4.3) between experimental and theoretical results, continuing the validity of the evaporation model.

#### 4.3 Evaluation of unknown $C_s(T)$ and $P_s(T)$ dependencies for pesticides

The reference data on vapour pressure-temperature dependencies for other studied pesticides (phosalone, ethaphos, propiconazole) are unavailable, but it is possible to evaluate them using experimental evaporation data (Table 1) and theoretical calculations (relations (24) or (24a). For this purpose the experimental and theoretical evaporation times for a particle of  $d_m = 2.03 \mu\text{m}$  must be assumed to be equal, and the reverse transformation of relationships (24) or (24a) must be performed. Such evaluated vapour-temperature

dependencies are listed below in standard reference forms  $C_s(T) \approx C_0 \exp(-H_{\text{eff}}/RT)$ , or  $P_s(T) \approx P_0 \exp(-H_{\text{tr}}/RT)$ ; here  $R \approx 8.3 \text{ J mole}^{-1} \text{ K}^{-1}$  is the molar gas constant;  $H_{\text{eff}}$  and  $H_{\text{tr}}$  are the effective and true latent heats,  $\text{kJ mole}^{-1}$ :

$$C_s(T) \approx 10^{6.43(\pm 0.80)} \exp(-100.85(\pm 5.4)/RT) \text{ g cm}^{-3}$$

$$P_s(T) \approx 10^{13.77(\pm 0.85)} \exp(-103.75(\pm 5.7)/RT) \text{ Pa}$$

for phosalone

$$C_s(T) \approx 10^{2.91(\pm 0.46)} \exp(-71.60(\pm 4.7)/RT)$$

$$P_s(T) \approx 10^{10.32(\pm 0.85)} \exp(-74.50(\pm 4.8)/RT)$$

for ethaphos

$$C_s(T) \approx 10^{3.74(\pm 0.43)} \exp(-82.85(\pm 2.9)/RT)$$

$$P_s(T) \approx 10^{11.15(\pm 0.45)} \exp(-85.95(\pm 3.0)/RT)$$

for propiconazole

As for propiconazole, a single reference vapour pressure is available ( $T_b = 180^\circ\text{C}$  at  $\approx 13.3 \text{ Pa}$ ),<sup>25</sup> and a comparison can be done,  $P_s(\text{eval.}) \approx 15.9 \text{ Pa}$ , against  $P_s(\text{ref.}) \approx 13.3 \text{ Pa}$ . A single datum is also available for ethaphos ( $T_b = 156^\circ\text{C}$  at  $\approx 33 \text{ Pa}$ ),<sup>25</sup> against  $P_s(\text{eval.}) \approx 16.8 \text{ Pa}$ . These results also confirm the validity of evaporation model, and that the model calculations coupled with the experimental technique described in this paper may be used to evaluate the unknown data on vapour pressure for various pesticides.

#### 4.4 Evaporation life-times of pesticide particles in atmosphere, and potential evaporation losses of pesticides from plant and soil surface

In Table 2 the estimated characteristic evaporation times (life-times) for pesticide particles are presented for potential atmospheric temperatures at heights up to 1–2 km above sea level, using the experimental data and the above theoretical relations. Such estimations are of course somewhat conditional, because the extrapolations of evaporation data from the experimental temperature range (50–120°C) to the ambient one (0–30°C) must cross the melting points for some pesticides studied. It is known, e.g. for parathion-methyl,<sup>24</sup> that the vapour pressure-temperature dependencies may be somewhat different below and above the melting point. Nevertheless, the differences are not great, and the above estimation of life-times might be adopted.

One should note from Table 2 that the particles of 1–20  $\mu\text{m}$  produced from a relatively volatile pesticide (malathion, parathion-methyl, ethaphos) can evaporate shortly after their production, at least at high daily temperature. As for less volatile substances (propiconazole phosalone), the aerosols may persist in the atmosphere for a long time. Due to these long life-times (tens or

**TABLE 2**  
Potential Evaporation Life-Times for Various Pesticide Aerosols under Ambient Conditions

Pesticide	Temperature (°C)	Evaporation life-time (h) Aerosol diameter (μm)			
		2	10	20	50
Malathion	0	0.5	12.8	51	320
	15	0.1	2.5	10	63
	30	0.02	0.5	2	13
Parathion-methyl	0	4.2	105	420	2600
	15	0.7	18	70	450
	30	0.13	3	12	75
Phosalone	0	296	7400	30000	190000
	15	29	725	2900	19000
	30	3	73	290	1900
Ethaphos	0	3.3	82	330	2000
	15	0.6	15	60	375
	30	0.12	3	12	70
Propiconazole	0	47	1175	4700	29000
	15	6.5	163	650	4200
	30	0.9	23	90	560

hundreds of days), the particles of 5–20 μm must be involved in the global wind transport of atmospheric pollutants as the commonly adopted characteristic times for such transport are 15–30 days.<sup>26</sup> The primary aerosols of 1–3 μm are mainly involved in the regional air transport, as such small particles usually evaporate after a few hours or days. The vapour will then be distributed in the atmosphere between free vapour and the vapour that is sorbed onto atmospheric particulate matter. Such secondary airborne pesticide matter will be transported long distance via the atmosphere, and it will take part in various processes of atmospheric chemistry and photochemistry. These problems are widely discussed,<sup>27,28</sup> but outside the scope of the present work.

As for large particles, 30–50 μm, they are mainly formed in the atmosphere after aerial or ground spraying upon fast evaporation of water out of 'pesticide + water' droplets followed by their dissipation in the air. However, the dry or wet deposition of such particles on land is very rapid,<sup>4,27,28</sup> and, hence, their long-distance air transport might be ignored. On the other hand, such particles form pesticide deposits on plant or soil surface on both treated fields and beyond the down-wind boundaries of the fields. For some time it has been recognized that highly volatile pesticides were lost from plant or soil surface mainly by vaporization into the atmosphere.<sup>29,30</sup> Moreover, it has been established that volatilization and vapour-phase air transport are important in the dissipation of even the so-called 'nonvolatile pesticides', such as DDT, some organochlorine and organophosphorus compounds (10–50% during 7–50 days).<sup>29</sup> The evaporation losses

for parathion-methyl, malathion and ethaphos deposits from some plants (wheat, cotton) have been measured as 50–70% during the first day after pesticide application.<sup>6, 31,32</sup> It seems that the estimated life-times for these substances (Table 2) are in agreement with the reference data, taking into account a high daily temperature of plant surface (30–40°C), and the sessile state of drops on the leaf surface.<sup>31,33</sup>

On the other hand, the data in Table 2 cannot be used to predict the rates of pesticide losses from the soil, as the pesticide is usually soil-incorporated. Volatilization is dependent on pesticide concentration in the soil, air and soil temperature, soil water content, degree of adsorption or interaction between the soil material and the pesticide, rate of pesticide diffusion in soil bulk, etc. Consequently, the estimated life-time in itself cannot be used to predict the long-term volatilization of soil-incorporated pesticides, together with pesticides which have penetrated leaf surfaces, or pesticides which are dissolved in superficial leaf oils or covered with soil dust.

## 5 SUMMARY

A simplified physicochemical evaporation model for vaporization of the pesticide constituent out of multi-ingredient particles is discussed. The appropriate evaporation expressions are derived, and experimental procedures are described for both the individual multi-ingredient particles and the polydisperse aerosol mixtures, taking into account the initial particle composition, pesticide vapour pressure-temperature dependence, aerosol polydispersity, laminarity of

'air + aerosols' flow in a hot tube vaporizer, and air temperature expansion. The temperature dependencies of evaporation rates for both the polydisperse aerosol mixtures and the individual particles of diameter  $d_m \approx 2.03 \mu\text{m}$ , and, then, of any particle diameter are determined. The unknown  $C_s(T)$  or  $P_s(T)$  dependencies, and the evaporation life-times of pesticide particles in the atmosphere are evaluated for some pesticides.

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